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(58) Field of search

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(54) Surface conversion coating solution based on molybdenum and phosphate compounds

(57) A chromate and ferricyanide free aqueous treating and conversion coating solution contains, as essential ingredients at least one titanium, zirconium, hafnium or cerium compound, a fluoride compound, a molybdenum compound and a phosphate compound and may have a pH up to 8. Metal surface coatings produced are corrosion resistant yet allow the adhesion thereto of paints, inks, lacquers and other overlaying coatings. The composition may be applied to aluminium, zinc or steel, eg beverage cans. The titanium, zirconium, hafnium or cerium compound may be present as a fluorotitanate, fluorozirconate, fluorohyafnate or fluorocerate, preferably in the amount 0.005-10 g/l. The fluoride may be present in an amount 0.001-10g/l, the molybdate in an amount 0.01-10 g/l, and the phosphate in an amount 0.01-100 g/l. The composition may also contain a nickel compound eg as chloride, carbonate, nitrate or sulphate, with the nickel present in an amount 0.01-10 g/l. Additional ingredients are sequestrants, eg sodium gluconate or heptogluconate, and surface active agents.

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At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

This print takes account of filing to enable the application to comply with the formal requirements of the Patents Rules 1990.

FIG 1 - Auger Depth Profile Plot of Sample 84.

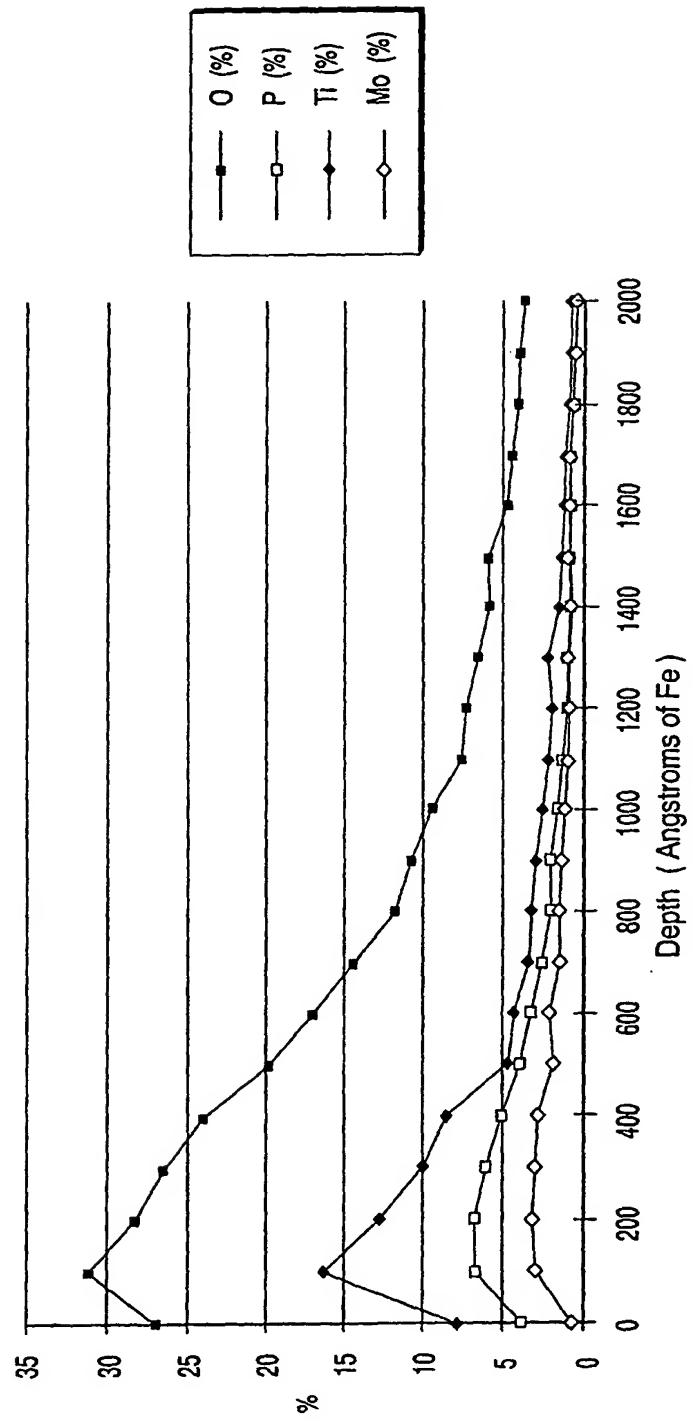
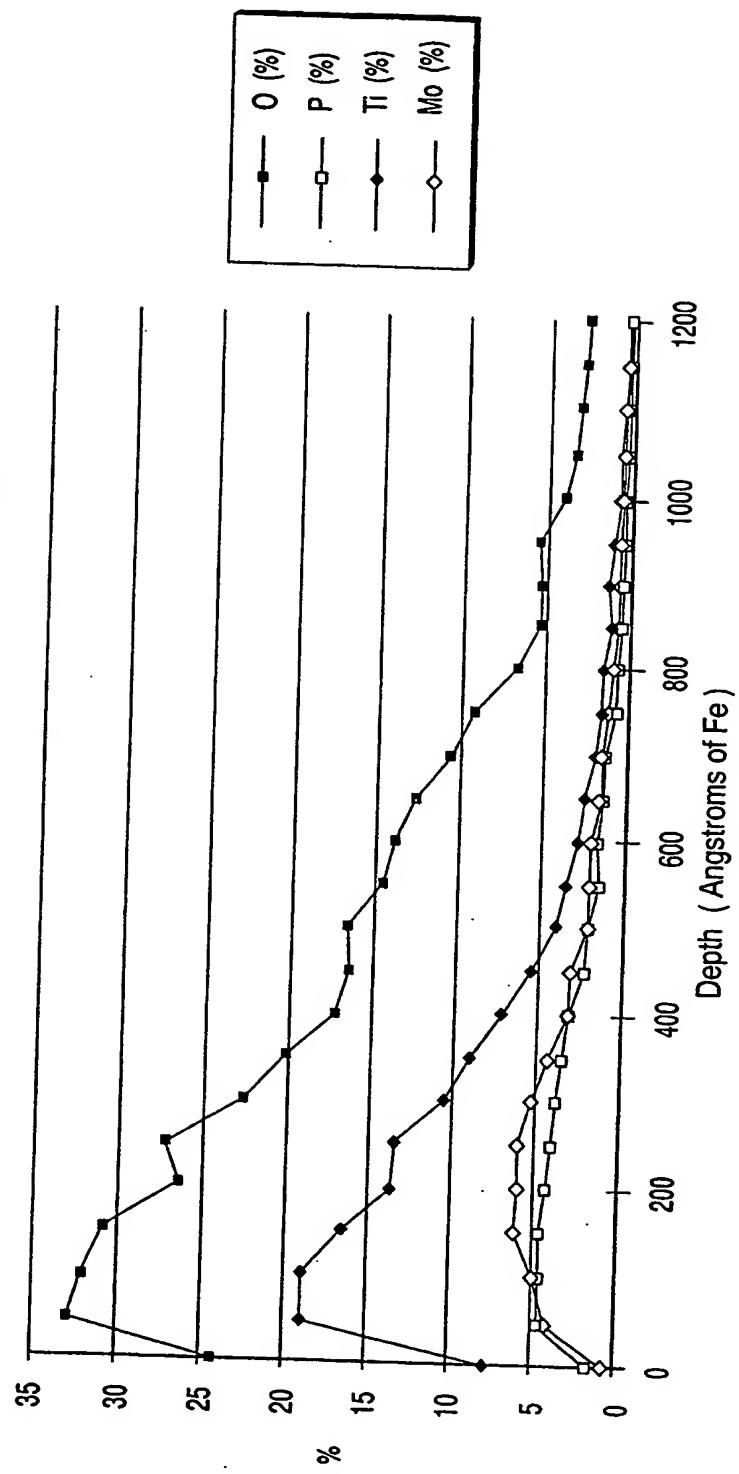


FIG 2 - Auger Depth Profile Plot of Sample 85.



SURFACE COATING SOLUTION

This invention relates to the application to metal surfaces of coatings which are corrosion resistant and to which paints, inks, lacquers and other overlying coatings adhere.

5 This invention particularly relates to aqueous coating solutions which are generally acidic and free of chromates and ferricyanide and which form the aforementioned types of coatings on aluminium and other metallic surfaces.

10 Corrosion resistant coatings such as those of the present invention find particular application in the manufacture of aluminium beverage cans and it will be with such application in mind that the following invention will be described. It will, however, be appreciated that the invention has broad application in the metal processing industry in general.

15 It is desirable, particularly in the manufacture of aluminium cans, that corrosion resistant coatings applied to aluminium surfaces do not alter the bright shiny appearance of the aluminium even though the final product may completely or partially be covered with overlying siccative coatings. The corrosion resistant coatings should preferably also have properties such that these overlying coatings adhere tightly thereto.

20 The corrosion resistant coatings should preferably also have the ability to withstand discolouration of the aluminium surface when subjected to hot water of about 65°C to about 75°C, referred to in the can industry as "Pasteurisation". This treatment can cause uncoated or inadequately coated aluminium surfaces to blacken or otherwise discolour. In addition to this property it is desirable that aluminium surfaces treated with these conversion coatings be able to undergo a simple testing procedure to confirm the presence of the coating. One such test employed in the can industry is known as the "muffle test". A sample of cleaned and treated aluminium surface is placed in a muffle furnace at about 25 550°C for about 5 minutes. The presence of the coating is indicated by a colour change of the aluminium surface.

30 Corrosion resistant coatings of the present invention can also find application in the treatment of steel surfaces and zinc and aluminium coated materials such as galvanised zinc coated or aluminium-zinc coated steels. The corrosion resistant coatings should preferably exhibit the ability to prevent the formation of white rust on zinc coated surfaces exposed to the atmosphere. Such coatings should preferably also have properties such that any overlying siccative coatings, such as for example, paints or lacquers, adhere tightly

thereto.

In order to prevent the formation of white rust on galvanised or zinc coated steel it is generally accepted that the treatment of a surface with a chromate imparts excellent anti corrosive properties at low cost. However the use of chromate is under constant 5 scrutiny with respect to pollution regulations, toxicity to exposed workers and disposal problems. Chromate treatments have a distinct disadvantage in that they provide for inferior adhesion of paint.

In another process, treatment of the zinc coated steel with a phosphate provides for improved paint adhesion thereto however corrosion resistance is inferior to the chromate 10 treated substrates.

Phosphate coatings, such as these, also find application in the treatment of steel, where they provide for excellent adhesion of siccative coatings. Coatings of this type however do not impart substantial anticorrosive properties to the treated metal surfaces and subsequent processing, such as for example, the absorption of protective oils onto the 15 phosphate coating or the use of a chromating dip may have to be employed in order to provide for adequate corrosion protection.

Phosphating processes for metals are well known and numerous patents have been established over the last 70 years. In essence, phosphating processes are relatively simple, comprising of mildly acidic phosphate solutions, with pH in the range of 3 to 5.5, and often 20 containing metal salts such as for example zinc salts, molybdenum salts, nickel salts or manganese salts.

Most phosphating solutions are proprietary mixtures and the processes are often known by their trade names. In general the processes provide coatings of complex metal phosphates on steel or zinc based alloys by treatment in or with a solution of acid 25 phosphates. The coatings provide for, in these proprietary formulations, good adhesion of siccative coatings. However they often do not provide for adequate corrosion protection without the need for subsequent anticorrosive processes such as for example the use of chromates.

Aqueous coating solutions which provide useful alternatives to chromate and 30 ferricyanide containing systems are known. However, such systems have limited appeal only since they require exploitation within a narrow range of operating parameters such as pH, temperature and contact times.

Accordingly it is an object of the present invention to provide an aqueous coating solution which is chromate and ferricyanide free and which can be applied within a less restrictive range of parameters such as pH, temperature and contact times.

It is a further object of the present invention to provide a process for treating metal  
5 surfaces with a chromate and ferricyanide free solution to produce a corrosion free coating.

In accordance with one aspect of the present invention, there is provided an aqueous treatment or coating solution which contains as essential ingredients at least one titanium, zirconium, hafnium or cerium compound; a fluoride compound; a molybdenum compound and a phosphate compound.

10 In accordance with a further aspect of the present invention there is provided a chromate and ferricyanide free aqueous coating solution containing between 0.01 and 100 g/l phosphate, between 0.001 and 10 g/l fluoride, between 0.01 and 10 g/l molybdate and one or more compounds of titanium, zirconium, hafnium or cerium in a total amount of between 0.005 to 10 g/l, in a pH range of from 0 to 8.

15 The solution of the present invention can be used to treat a bright shiny aluminium surface in manner such that the bright shiny appearance of the surface is not altered, while forming on the surface a uniformly colourless and clear coating which provides for corrosion resistance and to which overlay, for example, siccative coatings adhere. An aluminium surface treated in this manner is capable of undergoing the so-called "muffle  
20 test" to confirm the presence of the clean and colourless coating.

In accordance with another aspect of the present invention there is provided a process for producing a corrosion resistant coating, which comprises treating a metal surface with a chromate and ferricyanide free aqueous solution containing between 0.01 and 100 g/l phosphate, between 0.001 and 10 g/l fluoride, between 0.01 and 10 g/l molybdate,  
25 and one or more components of titanium, zirconium, hafnium or cerium in a total amount of from 0.005 to 10 g/l, at a pH of from 0 to 8. The treated metal surface is then rinsed with water or other convenient rinsing agent and dried by any convenient conventional means.

Prior to treating the metal surface with the coating solution it may be appropriate  
30 to pre-treat the metal surface with, for example, degreasers, alkali cleaners or acidic cleaning solutions.

In accordance with yet another aspect of the present invention there is provided a process for producing a corrosion resistant coating, which comprises treating a metal surface with a chromate and ferricyanide free aqueous solution containing between 0.01 and 100 g/l phosphate, between 0.001 and 10 g/l fluoride, between 0.01 and 10 g/l molybdate, 5 between 0.01 and 10 g/l nickel, and one or more components of titanium, zirconium, hafnium or cerium in a total amount of from 0.005 to 10 g/l at a pH of from 0 to 8.

The incorporation of nickel into the aqueous coating solution provides for improved coating times in situations where the surface to be coated contains a high percentage of zinc, as for example, die-cast metals or galvanised parts. The inclusion of nickel salts in 10 the coating solution will typically reduce contact times by as much as 50% in certain circumstances.

The corrosion resistant properties of coatings formed from coating solutions within the scope of the present invention include the ability to withstand blackening or discolouration of an aluminium surface when subjected to a "pasteurisation test" of hot 15 water having a temperature of 65°C to about 75°C, at a pH of 8.8 to 9.1 for a period of time at least 20 minutes up to as long as 30 minutes and the ability to prevent the occurrence of white-rust formation of on zinc or aluminium/zinc alloy coated steel surface when exposed to the atmosphere for a period of time of at least 30 days up to as long as 90 days or more.

20 The coating solutions of the present invention are capable of effectively forming the aforementioned types of coatings in the absence of hexavalent chromium and materials such as ferricyanide and ferrocyanide. In addition the coating process has been found to be tolerant of a variety of surface cleaning procedures used prior to the coating stage and is capable of providing a primary cleaning action.

25 The coating solutions of the present invention can be prepared from a variety of source compounds which contain the aforementioned essential ingredients (ie a titanium, zirconium, hafnium and/or cerium compound, a fluoride compound, a molybdenum compound and a phosphate compound) and which are soluble in the solution.

30 The source of the titanium, zirconium, hafnium or cerium can be, for example, the ammonium and alkali metal salts of fluotitanates, fluozirconates and fluohafnates and also the metallic fluorides. In addition the coating solutions can be prepared from a mixture of soluble compounds of which one contains titanium, zirconium, hafnium or cerium, such as for example, water soluble sulphate or nitrate salts and the other of which contains fluoride.

As to the source of molybdenum there can be used soluble molybdate compounds such as for example molybdic acid and sodium molybdate.

Satisfactory coatings can be produced from coating solutions containing as little as about  $4 \times 10^{-4}$  molar of either titanium, zirconium, hafnium or cerium (about 0.02 g/l Ti, 5 about 0.05 g/l Zr, about 0.09 g/l of Hf and about 0.07 g/l of Ce) and about  $5 \times 10^{-4}$  molar molybdenum (about 0.05 g/l Mo). In coating solutions which utilise a mixture of Ti, Zr, Hf or Ce, the total amounts of these metals should be at least about  $4 \times 10^{-4}$  molar. The amounts of these ingredients, however, may be required to be increased in order to produce satisfactory coatings depending on other parameters of the coating process as will be 10 discussed below.

Titanium, zirconium, hafnium or cerium can be used in amounts up to their solubility in the acidic aqueous coating solution. The solubility limits of the ingredients will depend on other parameters of the coating solution, including particularly, the amount 15 of fluoride in the coating solution. These parameters should be controlled such that the formation of titanium, zirconium, hafnium or cerium precipitates are avoided. The formation and accumulation of any type of precipitate in the coating solution is undesirable and will tend to interfere with the application of the coating, cause deposition on the coated metal surface, which can adversely affect coating properties, and cause the clogging of spray nozzles in spray applications.

20 The coating solution of the present invention can be formulated in such a way, as for example, by the incorporation of dissolved nickelous salts or manipulation of the various parameters of the coating process, such that a mixture of metal types may process through the same coating solution and effectively forming the aforementioned types of coatings in the absence of hexavalent chromium and materials such as ferricyanide and 25 ferrocyanide.

The incorporation of soluble nickelous salts into the coating solution of the present invention at between 0.01 and 10 g/l nickel will, in certain circumstances, afford improved coating times where particular metals or metal alloys such as for example zinc or iron, are to be contacted.

As to the source of the nickel there can be used, for example, soluble nickelous compounds such as water soluble chlorides, carbonates, nitrates and sulphates.

As to the fluoride concentration, the minimum concentration should be that which is sufficient to combine with all the titanium, zirconium, hafnium or cerium present to form 5 a water soluble complex therewith, for example, a fluotitanate, fluozirconate, fluohafnate or fluocerate. The formation of these soluble complexes deter or prevent the formation of titanium, zirconium or hafnium precipitates.

Several other considerations should be taken into account with respect of fluoride concentration in the coating solutions. The coating solution of the present invention will 10 dissolve the substrate metal, for example, aluminium or zinc and a gradual build-up of dissolved aluminium or zinc will occur. To prevent or deter any adverse affects of the build-up of these metals in solution on the coating process, the coating solution should contain sufficient fluoride to complex the dissolved metals. The amount of fluoride required will depend on the degree to which dissolved metal builds-up in the coating 15 solution and will be dependent on various factors such as, for example, the method by which the solution is contacted with the metal substrate or alloy and the shape of the surface being treated.

As to the source of flouride any material which can provide flouride and which is soluble in the coating solution may be used provided it does not contain a constituent 20 which may adversely affect the coating process. Materials such as hydrofluoric acid and its salts, alkali metal bifluorides,  $H_2SiF_6$  or  $HBF_4$ , may be used as well as complex fluorides of titanium, zirconium, hafnium or cerium. However if the latter fluoride complexes are used there should be added to the coating solution additional material which is a source of fluoride for complexing the aluminium or zinc that builds up during continuous use.

25 The pH of the coating solution can vary over a wide range, for example, from about 1 to about 8. At higher pH's phosphate precipitation can be a problem. Preferably, a pH within the range of about 1.0 to about 5.0 is used. The pH of the solution may be adjusted by using appropriate amounts of phosphoric acid, nitric acid, sulphuric acid or any acid which will not adversely affect the coating process.

The temperature of the coating solution should be such that the reactive ingredients of the solution bond to the metal surface. The coatings can be applied to the metal surface over a wide temperature range of from 0°C up to about 95°C. Preferably from room temperature up to about 90°C. A temperature range of about 40°C to about 80°C is  
5 particularly preferred. The temperature of application is dependent on various parameters of the coating operation including, for example, the contact time of the solution with the metal surface, the type of metal to be coated and the reactivity of the solution which in turn depends on the pH and concentration of ingredients in the coating solution.

The coating solution should be applied to a clean metal surface. Available cleaning  
10 compositions such as alkaline or acidic cleaning solutions can be used to clean the metal surface according to conventional techniques prior to the coating application.

The coating solution can be formulated in such a way, as for example, by the addition of surface active agents, such that a primary cleaning action can be provided. The surface active agents employed to provide the cleaning action of the coating solution should  
15 be present in sufficient concentration such that surface soils, for example, drawing lubricants and protective oils, can be readily removed. The choice of surface active agents should be such that the coating process is not adversely affected and the cleaning action is adequately provided. Surface active agents, such as for example, nonyl phenol alkoxylates, octylphenyl, alkoxylates, oxyethylene glycol rosin esters and propoxylated  
20 alcohol ethoxylates can readily be employed. When employed, the surface active agents will be in the range of from 0.01 to 100 g/l.

Other additives used as sequesterants may be added to the coating solution formulation. Such agents assist in maintaining dissolved metal ions in solution. When added, such sequestering agents may be employed in the range of from 0.05 to 50 g/l.  
25 Preferred sequestering agents include polyhydroxy compounds having up to 7 carbon atoms such as sodium gluconate or heptogluconate.

The thickness of the coating formed on the metal surface is dependent on a number of parameters including solution contact time, temperature, type of metal being processed, concentration and pH. In the case of aluminium, for example coating weights of about 120

g/m<sup>2</sup> are typically desired. In the case of steel, for example, coating weights of from 300 mg/m<sup>2</sup> to 1000 mg/m<sup>2</sup> are typically required for applications where siccative coatings such as for example, paints or lacquers, are to be applied. Coating weights of up to 1500 mg/m<sup>2</sup> or more may be desired in certain specific circumstances. Determination of contact times 5 necessary to produce coating thicknesses within these aforementioned ranges will have to be made on a case by case basis. In general, contact times of from about 2 seconds to about 60 seconds will be required with coating times of up to about 120 seconds or more being used in some circumstances.

Once the conversion coating has been applied to the metal surface, it is rinsed with 10 water and dried by conventional means, such as by passage through an oven. An overcoat of paint, ink, lacquer, plastic resin, either water or solvent borne or organic coatings provided for by powder coating methods may then be applied by conventional techniques.

The coating solution of the present invention can be prepared conveniently by dilution of an aqueous concentrate of the ingredients with an appropriate amount of water.

15 In a continuous coating operation, it is important to properly replenish the solution in order to maintain the effectiveness of the coating process. Various ingredients comprising the solution are depleted as a result of reactions which take place during the formation of the coating. These ingredients must be replenished by either monitoring the amounts of each individual ingredient in the coating solution and adding it as it is depleted 20 or it can be accomplished by adding an aqueous concentrate of the ingredients in such a ratio as to maintain the effectiveness of the coating solution.

#### Examples

The examples below are illustrative of the practice of the present invention and are not intended to be limiting or exhaustive thereof.

25 The aluminium surfaces treated with the solutions identified in the examples, unless otherwise stated, were drawn aluminium cans which were first degreased, as necessary, in an acidic aqueous cleaning solution consisting of sulphuric acid, fluoride and detergents and then rinsed in free flowing tap water. The coating solutions were then applied by immersion techniques as set out below. After treatment with the identified solutions the

aluminium surfaces were rinsed in free flowing tap water and dried in an oven at 110°C for about 2 minutes.

The following tests were employed to evaluate the relative degree of coating present and the corrosion resistance of the treated aluminium surface.

5    Muffle Test

A clean and treated can is placed in a muffle furnace at 550°C for about 5 minutes. The presence of the coating is indicated by a light yellow, through golden brown, to a dark purple-brown discolouration, depending on the amount of coating present.

This type of test is conveniently used as a simple and efficient on-line procedure  
10 to estimate the coating weights present on production items. The colour intensity of the coated aluminium surface being in proportion to the coating thickness.

Pasteurisation Test

A clean and treated can is immersed in a water bath containing 0.3 g/l sodium borate and 0.1 g/l potassium fluoride at a pH range of 8.8 to 9.1 for a period of about 30  
15 minutes at 65-70°C. After immersion the cans are rinsed with free flowing tap water and allowed to dry before examination for presence of staining effects.

A cleaned only can, when subjected to this form of test, rapidly turns a black or brown colour. It will be seen from the following examples below that treatment of the aluminium surfaces with the coating solutions of the present invention resulted in surfaces  
20 which were not blackened or otherwise discoloured or which resisted blackening or other discolouration when subjected to the pasteurisation test. The results of the tests were rated out of 10 as follows: 10, perfect, no blackening; 7, acceptable and 0, total failure, severe blackening.

Table 1 below demonstrates the interdependence of molybdenum and titanium levels  
25 on coating formation and water stain resistance (pasteurisation test) of aluminium surfaces. Phosphate was present in the solution at 9 g/l (as PO<sub>4</sub><sup>3-</sup>), fluoride present at 1.3 g/l. Bath temperature was held at 60°C with a contact time of 10 seconds at a pH of 2.

Table 1

Sample number	Mo conc. (g/l)	Ti conc. (g/l)	Muffle Test Colour	Pasteurisation test
1	0.28	0.07	light	4
2	0.28	0.10	golden brown	10
3	0.15	0.10	light	2
4	0.28	0.17	golden brown	10

Table 2 demonstrates the dependence of the coating formation and muffle test colouration of aluminium surfaces on levels of phosphate present in solution. The cans were immersed for 10 seconds at a temperature of 60°C and the solution made up to contain  $\text{SO}_4^{2-}$  at 4.8 g/l, F<sup>-</sup> at 0.9 g/l, Mo at 0.18 g/l, Ti at 0.07 g/l. The solution was maintained at a pH of 2.

Table 2

Sample number	Phosphate conc. (g/l)	Muffle test colour
5	0	none
6	0.2	very light tan
7	0.4	golden brown
8	1.0	golden brown

Table 3 demonstrates the broad pH range under which coatings can be applied to aluminium surfaces. The coatings were applied by immersion at 60°C. The solution was made-up to contain  $\text{PO}_4^{3-}$  at 3 g/l, F<sup>-</sup> at 0.45 g/l, Mo at 0.09 g/l and Ti at 0.05 g/l. The coated aluminium was subjected to the muffle test as an indication of coating weight.

Table 3

Sample number	pH	Contact time (seconds)	Muffle test colour
5			
	9	1.8	golden brown
	10	2	golden brown
	11	2.5	golden brown
	12	3	golden brown
10	13	3.5	golden brown
	14	4	golden brown
	15	5	golden brown

Table 4 demonstrates the broad temperature ranges under which the coating may be applied to the aluminium surface. The coating solution was made-up to contain  $\text{PO}_4^{3-}$  at 15 4.8 g/l,  $\text{F}^-$  at 0.9 g/l, Mo at 0.18 and Ti at 0.07 g/l. The pH of the solution was maintained at 2.

Table 4

Sample number	Temperature (°C)	Contact time (seconds)	Muffle Test colour
20			
	16	0	pale yellow
	17	5	light tango
	18	10	light tan
25	19	15	light tan
	20	20	light tan
	21	30	golden brown
	22	40	golden brown
	23	50	golden brown
30	24	55	golden brown
	25	60	dark brown
	26	65	dark brown
	27	70	very dark brown
	28	80	purple brown
35	29	90	purple brown

Table 5 demonstrates the effect of contact times on the aluminium coating at 50 and 60°C. The solution was made up to contain 3 g/l  $\text{PO}_4^{3-}$ , 0.45 g/l F<sup>-</sup>, 0.09 g/l Mo and 0.05 g/l Ti. The pH of solution was maintained at 2.

Table 5

5

	Sample number	Temperature (°C)	Contact Time (seconds)	Muffle Test colour
10	30	60	2	golden brown
	31	60	5	golden brown
	32	60	10	golden brown
	33	60	15	dark brown
	34	60	20	purple brown
15	35	50	2	light tan
	36	50	5	golden brown
	37	50	10	golden brown
	38	50	15	golden brown
	39	50	20	dark brown

20

Table 6 demonstrates the concentration dependence on coating formation on aluminium surfaces and corrosion resistance. A concentrate of coating solution was made-up to contain 160 g/l  $\text{PO}_4^{3-}$ , 2.3 g/l F<sup>-</sup>, 2g/l Ti and 5 g/l Mo at a pH of 1.8 and applied to the aluminium surface at varying concentrations by immersion, at 60°C for 10 seconds.

Table 6

5	<u>Sample number</u>	<u>Dilution of concentrate</u> (% volume)	<u>Muffle</u> test	<u>Pasteurisation</u> test
	40	6%	dark	10
	41	4	golden brown	10
	42	2	golden brown	10
	43	1	light brown	9

10 Table 7 demonstrates that the coating formation on the aluminium surface will form in the presence of surface active agents such as gluconates and surfactants. The solution was made up to contain 3 g/l  $\text{PO}_4^{3-}$ , 0.45 g/l F<sup>-</sup>, 0.09 g/l Mo and 0.05 g/l Ti. The pH of the solution was maintained at 2, with a temperature of 60°C.

Table 7

15	Sample Number	Gluconate (g/l)	Surfactant 1* (g/l)	Surfactant 2* (g/l)	Muffle test	Contact time (sec)
20	44	1	-	-	golden brown	10
	45	1	-	-	golden brown	15
	46	-	0.1	0.1	grey brown	10
	47	-	0.1	0.1	grey brown	15
	48	-	0.2	0.2	tan	10
25	49	-	0.2	0.2	tan	15
	50	-	0.3	0.3	brown	10
	51	-	0.3	0.3	brown	15
	52	-	0.4	0.4	brown	10
	53	-	0.4	0.4	brown	15

30 \*Surfactant 1 is Teric GNS (ICI Aust)

\*Surfactant 2 is Teric 160 (ICI Aust)

Table 8 demonstrates that the coating solution can also be used to clean and form coatings on aluminium surfaces in a single phase process. A concentrate of the cleaning/coating solution was made-up to contain 160 g/l  $\text{PO}_4^{3-}$ , 2.3 g/l F<sup>-</sup>, 2 g/l Ti, 5 g/l Mo, 20 g/l Teric 164 (registered trademark of ICI Australia) and 25 g/l Teric RA 1315 (registered trademark of ICI Aust). A pH of 2 was maintained in the diluted solutions at a temperature of 60°C.

Table 8

10	Sample number	Dilution of concentrate (% volume)	Contact time (seconds)	Muffle Test colour
	54	2	10	brown
	55	2	20	brown
	56	4	10	purple brown
15	57	4	15	purple brown
	58	4	20	purple brown

It can also be demonstrated that the coating solution can also be used to form coatings on steel surfaces.

Coating weights of steel specimens coated with the coating of the present invention 20 may be determined using conventional procedures. The coated specimen to be analysed is carefully weighed on an analytical balance and immersed for 5 minutes in a 50 g/litre chromic acid solution at 74°C. The specimen is then rinsed thoroughly in hot water and quickly dried. The specimen should then be re-weighed immediately. The weight difference divided by the surface area of the specimen is the calculated coating weight.

25 Table 9 demonstrates the temperature ranges under which the coating may be applied to steel surfaces. The coating solution was made-up to contain  $\text{PO}_4^{3-}$  at 8 g/l, F<sup>-</sup> at 2.5 g/l, Mo at 0.25 g/l and Ti at 0.1 g/l. The pH of solution was maintained at 2.

Table 9

	Sample Number	Temperature (°C)	Contact (seconds)	Coating weigh (mg/m <sup>2</sup> )
5	59	35	300	530
	60	45	120	400
	61	55	120	800
	62	65	120	1250
10	63	75	120	2050
	64	85	120	2050

Table 10 demonstrates the effect of contact time on the steel coating at 55 and 65°C. The solution was made up to contain 8 g/l PO<sub>4</sub><sup>3-</sup>, 2.5 g/l F<sup>-</sup> 0.25 g/l Mo and 0.1 g/l Ti. The pH of solution was maintained at 2.

15

Table 10

	Sample Number	Temperature (°C)	Contact time (minutes)	Coating weigh (mg/m <sup>2</sup> )
20	65	55	1	560
	66	55	2	800
	67	55	5	1550
	68	65	1	670
	69	65	2	1250
25	70	65	5	2510
	71	65	10	3490

Table 11 demonstrates the concentration dependence on coating formation on steel surfaces. A concentrate of coating solution was made up to contain 160 g/l PO<sub>4</sub><sup>3-</sup>, 2.3 g/l F<sup>-</sup>, 2 g/l Ti and 5 g/l Mo at a pH of 1.8 and applied to the metal surface by immersion at varying concentrations at the stated temperatures for 5 minutes.

Table 11

	Sample Number	Dilution of concentrate (% volume)	Temperature (°C)	Coating weight (mg/l)
5	72	1	55	480
	73	1	65	530
	74	1	75	750
10	75	2	55	610
	76	2	65	750
	77	2	75	1150
	78	5	35	530
	79	5	45	830
15	80	5	55	1550
	81	5	65	2510
	82	5	75	3250
	83	5	85	3440

The conversion coatings applied to aluminium surfaces, using the coating solutions  
20 of the present invention, were analysed by scanning electron microscopy techniques and found to contain, as integral components of the surface thus formed, molybdenum, titanium and phosphorus in the approximate atomic ratio of 2 : 3 : 5 respectively. The ratio of these essential elements of the coating appeared constant within the broad range of solution operation parameters such as pH, temperature and contact times.

25 Figures 1 and 2, below, illustrate the Auger depth profile of aluminium and zinc alloy coated steel surfaces immersed in a coating solution of the present invention as set out below.

Sample 84, as analysed by Auger techniques, is an aluminium surface immersed for 10 seconds at a temperature of 60°C in a coating solution made-up to contain 4.8 g/l PO<sub>4</sub><sup>3-</sup>,  
30 0.9 g/l F<sup>-</sup>, 0.18 g/l Mo and 0.07 g/l Ti at a pH of 2. As can be seen from the plot P, Ti

and Mo are present as essential components of the coating thus formed on the aluminium surface.

Sample 85, as analysed by Auger techniques, is a zinc/aluminium alloy coated steel surface immersed for 5 seconds at a temperature of 60°C in a coating solution made up to contain 6.5 g/l PO<sub>4</sub><sup>3-</sup>, 2 g/l F, 0.25 g/l Mo, 0.09 g/l Ti and 0.2 g/l Ni. As can be seen from the plot P, Ti and Mo are present as essential components of the coating so formed on the metal surface. The presence of nickel in the coating solution, which provides for improve coating times, is not directly incorporated into the coating.

Coating weights of the coatings of the present invention on zinc alloy coated steel can be determined by immersing a clean, accurately weighed sample in a solution of 20 g/l ammonium dichromate and 280 g/l ammonium hydroxide for 4 minutes at 21°C. The sample should then be rinsed in hot water and immediately dried. The sample is then re-weighed and the difference in weight divided by the sample surface area calculated to give the coating weight.

Table 12 demonstrates the improvement of coating formation by the coating solution on zinc or zinc alloy coated steel when nickel is incorporated into the formulation. Zinc or zinc alloy coated steel samples immersed in a coating solution made up to contain 6.4 g/l PO<sub>4</sub><sup>3-</sup>, 1.2 g/F, 0.25 g/l Mo and 0.09 g/l Ti for 5 seconds at 60°C were analysed for coating weights at varying Ni concentrations as indicated below.

20

Table 12

	Sample Number	Alloy coating on steel	Ni concentration (g/l)	Coating weight (mg/m <sup>2</sup> )
25	86	Zinc / Aluminium	0	240
	87	Zinc / Aluminium	0.25	360
	88	Galvanised	0	150
	89	Galvanised	0.25	280

From the above examples it can be demonstrated that the present invention provides a coating solution which permits the formation of a conversion coating on the surface of aluminium in a manner such that the bright shiny surface of the aluminium is unaltered. The coated surface has the ability to withstand discolouration when subjected to 5 pasteurisation and to which overlying siccative coatings adhere. The coating solution exhibits the capacity to be tolerant of incomplete precleaning processes and has the ability to clean and coat metal surfaces in a single step operation.

It can also be demonstrated from the foregoing examples that the present invention provides a coating solution which permits the formation of a conversion coating on the 10 surface of steel and galvanised or zinc and zinc alloy coated steel. The coated surface has the ability to withstand corrosion and improve the adhesion of overlying siccative coatings.

CLAIMS

1. A chromate and ferricyanide free aqueous treating and coating solution which comprises essentially at least one titanium, zirconium, hafnium or cerium compound; a fluoride compound; a molybdenum compound; and a phosphate compound.
- 5 2. A treating and coating solution according to claim 1 which comprises essentially 0.01 to 100 g/l phosphate, 0.001 to 10 g/l fluoride, 0.01 to 10 g/l molybdate, and one or more of the compounds of titanium, zirconium, hafnium or cerium in a total amount of from 0.005 to 10 g/l, in the pH range 0-8.
- 10 3. A treating and coating solution according to claim 2 which comprises essentially 0.01 to 100 g/l phosphate, 0.001 to 10 g/l fluoride, 0.01 to 10 g/l molybdate and 0.005 to 10 g/l.
4. A treating and coating solution according to any one of the preceding claims which further includes a nickel compound wherein nickel is present in the solution in the range of from 0.01 to 10 g/l.
- 15 5. A treating and coating solution according to any one of the preceding claims which further includes a sequesterant in the range of 0.05 to 50 g/l.
6. A treating and coating solution according to claim 5 wherein the sequesterant is sodium gluconate or heptogluconate.
- 20 7. A treating and coating solution according to any one of the preceding claims which further includes a surface active agent in the range of from 0.01 to 100 g/l.
8. A treating and coating solution according to claim 7 wherein the surface active agent is selected from one or more of the group consisting of nonyl phenol alkoxylates, oxyethylene glycol rosin esters, propoxylated alcohol ethoxylates, and octylphenyl alkoxylates.

9. A process for providing a corrosion resistant coating to a metal surface which process comprises the sequential steps of:

5                     (a) treating the metal surface with a chromate and ferricyanide free solution consisting essentially of at least one titanium, zirconium, hafnium or cerium compound, a fluoride compound, a molybdenum compound and a phosphate compound at a temperature within the range of from 0°C to about 95°C for a contact time sufficient to provide a corrosion resistant coating to said metal surface, the pH of said coating solution being maintained in the range of from 0 to 8,

10                   (b) rinsing said coated metal surface with water or other convenient rinsing agent, and

                     (c) drying the coated metal surface.

10. A process according to claim 9 wherein the coating solution contains from 0.01 to 100 g/l phosphate, 0.001 to 10 g/l fluoride, from 0.01 to 10 g/l molybdate, and one or more titanium, hafnium, zirconium or cerium compound in a total amount of from 0.005 to 15      10 g/l.

11. A process according to claim 10 which comprises, in addition to the phosphate, fluoride and molybdate, a titanium compound in the range of from 0.005 to 10 g/l.

12. A process according to claim 11 wherein the titanium compound is replaced either in full or in part by either one or more of hafnium, zirconium or cerium.

20      13. A process according to any one of claims 9 to 12 wherein the coating solution further comprises a nickel compound in the range of from 0.01 to 10 g/l.

14. A process according to any one of claims 9 to 13 wherein the coating solution further includes a sequesterant in the range of from 0.05 to 50 g/l.

15. A process according to claim 14 wherein the sequesterent in a polyhydroxy compound having up to 7 carbon atoms.
16. A process according to any one of claims 9 to 15 wherein the coating solution further includes a surface active agent in the range of from 0.01 to 100 g/l.
- 5 17. A process according to claim 16 wherein the surface active agent is selected from one or more of the group consisting of nonyl phenol alkoxylates, propoxylated alcohol ethoxylates, octyl phenyl alkoxylates and oxyethylene glycol rosin esters.
18. A process according to any one of claims 9 to 17 wherein the metal surface treated is aluminium, aluminium alloy, zinc, zinc alloy or steel.
- 10 19. A process according to claim 18 wherein the metal surface treated is aluminium cans or can stock.
20. A process according to any one of claims 9 to 19 wherein the metal surface is pretreated with an alkaline or acidic cleaning agent.
- 15 21. A process according to any one of claims 9 to 20 wherein the treating and coating solution is applied to the metal surface by spraying, immersion or rolling.
22. A process according to any one of claims 9 to 21 which includes the further step of applying to said coating an overlying siccative coating by a water borne solution which may contain a polyester.
- 20 23. A metal surface having a corrosion resistant coating whenever applied by a process according to any one of claims 9 to 22.
24. A chromate and ferricyanide free aqueous treating and coating solution and process for providing a corrosion resistant coating to a metal surface, substantially as hereinbefore described with reference to any one or more of the examples.

Relevant Technical fields		Search Examiner
(i) UK CI (Edition K )	C7E; C7V	P G BEDDOE
(ii) Int CI (Edition 5 )	C23C	
<b>Databases (see over)</b>		Date of Search
(i) UK Patent Office		21 OCTOBER 1992
(ii) ONLINE DATABASE: WPI		

Documents considered relevant following a search in respect of claims 1-24

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
Y	GB 2131052 A (PYRENE) see especially Tables 1, 2	1,2,9,10, 11,12
Y	GB 2014617 A (PYRENE) see especially Examples 1, 3	1,2,9,10 11,12
Y	GB 1373129 A (COLLARDIN) see especially page 2 lines 3-53	1,4,9
Y	GB 1198546 A (PYRENE) see especially page 1 lines 64-70	1,2,4,9, 10,11,12
Y	GB 1193460 A (COLLARDIN) see especially page 1 line 54 - page 2 line 18	1,4,9
Y	GB 1093119 A (PYRENE) see especially page 1 line 66 - page 2 line 2; Example 1	1,2,4,9, 10,11,12
X	GB 1083779 A (PYRENE) see especially page 1 lines 43-66	1,9
Y	GB 900825 A (AMCHEM) see especially Example VI	1,2,4,9, 10,11,12
X	US 4264378 A (OXYMETAL) see especially Example 6	1,2,4,9, 12,13

Category	Identity of document and relevant passages	Relevant to claim(s.)

### Categories of documents

X: Document indicating lack of novelty or of inventive step.

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E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

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